

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 974 571 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
23.04.2003 Bulletin 2003/17

(51) Int Cl.7: **C07C 17/25**

(21) Application number: 99305781.9

(22) Date of filing: 21.07.1999

(54) Preparation of 1,1,1,3-tetrafluoropropene (1234ze)

Herstellung von 1,1,1,3-Tetrafluorpropen (1234ze)

Préparation du 1,1,1,3-tétrafluoropropène (1234ze)

(84) Designated Contracting States:

AT BE CH DE DK ES FR GB GR IE IT LI NL PT SE

(30) Priority: 21.07.1998 US 119560

(43) Date of publication of application:
26.01.2000 Bulletin 2000/04

(73) Proprietor: ATOFINA CHEMICALS, INC.
Philadelphia PA 19102-3222 (US)

(72) Inventors:

- Elsheikh, Maher Yousef
Wayne, Pennsylvania 19087 (US)
- Fellenger, Paul David
Narvon, Pennsylvania 17555 (US)

(74) Representative: Stoner, Gerard Patrick et al
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

(56) References cited:

EP-A- 0 234 002	EP-A- 0 486 333
WO-A-96/05157	WO-A-96/41679
WO-A-98/33756	US-A- 3 499 048
US-A- 3 579 595	

- KNUNYANTS I L ET AL: "REACTIONS OF FLUORO OLEFINS. COMMUNICATION 13. CATALYTIC HYDROGENATION OF PERFLUORO OLEFINS" BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR, DIVISION OF CHEMICAL SCIENCES, 1 January 1960 (1960-01-01), pages 1312-1317, XP000578879 ISSN: 0568-5230
- DEPUY, C.H. & SCHULTZ, A.L.: "Electronic Effects in Elimination reactions. VIII. E2 Reaction of 2-Arylethyl Fluorides" JOURNAL OF ORGANIC CHEMISTRY, vol. 39, no. 7, 5 April 1974 (1974-04-05), pages 878-881, XP002118546
- PATENT ABSTRACTS OF JAPAN vol. 003, no. 152 (C-067), 14 December 1979 (1979-12-14) & JP 54 130507 A (DAIKIN IND LTD), 9 October 1979 (1979-10-09)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 974 571 B1

Description

[0001] This invention relates to preparation of cis/trans 1,1,1,3-tetrafluoropropene ("1234ze"), a monomer useful for the preparation of various homopolymers and copolymers, particularly to processes for the dehydrofluorination of 1,1,1,3,3-pentafluoropropane ("245fa"), a known blowing agent, to 1234ze using a chromium-based catalyst. While the prior art, R. N. Haszeldine, J. Chem. Soc., 1952 (3490), describes the synthesis of cis/trans 1,1,1,3-tetrafluoropropene by fluorination of 1,1,1-trifluoro-2-propyne, this latter feed stock material is not available commercially. Knunyants et al, in Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences 1960 pages 1312 to 1317, incidentally describe a conversion of 1,1,1,3,3-pentafluoropropane to 1234ze using KOH powder suspended in ether.

[0002] We propose herein a process for the preparation of 1234ze by contacting 245fa with a chromium-based catalyst and recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.

[0003] In the prior art, WO96/05157 proposes a Cr_2O_3 catalyst for use in dehydrofluorination reactions, exemplified by the preparation of trifluoroethylene from 1,1,1,2-tetrafluoroethane. Other chromium catalyst disclosures include EP234002, which uses chromium oxyfluoride to convert 1,1,1-trifluoro compounds to 1,1-difluoro compounds, and WO96/41679 and JP-A-54/130507, which use a fluorided Cr_2O_3 catalyst to convert 1,1-difluoroethane to vinyl fluoride and vinylidene fluoride respectively.

[0004] The process of the present invention comprises a process for the preparation of cis/trans 1,1,1,3-tetrafluoro-2-propene which comprises (a) contacting 1,1,1,3,3-pentafluoropropane with an oxygen-containing gas in the presence of a fluorided catalyst selected from Cr_2O_3 and $\text{Cr}/\text{Ni}/\text{AlF}_3$, and (b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.

[0005] The catalyzed process is preferably carried out in the gas phase. Use of the oxygen-containing gas such as air is to extend the catalyst lifetime, the level of oxygen generally being from about 1 to about 10 volume percent (preferably about 2 to 5%), based on the volume of the organic feed. Temperatures of from about 100°C. to about 600°C. are typically used, preferably from about 300°C. to about 400°C. The pressure can be atmospheric. Contact time (total flow rate per catalyst volume) is typically from about 1 to about 60 seconds, preferably from about 20 to 50 seconds. The catalyst is a fluorided chromium-based catalyst such as fluorided chromium oxide, Cr_2O_3 , which chromium-based catalyst is either unsupported or supported on a support such as activated carbon, graphite, fluorided graphite or fluorided alumina, the chromium catalyst being used alone or in the presence of a co-catalyst selected from

a nickel, cobalt, manganese or zinc salt. Two such preferred chromium catalysts are high surface area chromium oxide and chromium/nickel on fluorided alumina ($\text{Cr}/\text{Ni}/\text{AlF}_3$), preparation of this latter catalyst being taught, for example, in European Patent 486333. The chromium-based catalysts are preferably activated before use, typically by a procedure wherein the catalyst bed is heated to about 370°-380°C. (normally with a continuous flow of nitrogen), after which a mixture of approximately equal volumes of HF and air or nitrogen (preferably nitrogen) are fed over the catalyst bed for about 18 hours.

[0006] The following examples are illustrative.

[0007] Example 1. 52.4 Grams of a high surface area Cr_2O_3 catalyst was activated by first feeding 30 ccm of nitrogen for 2 hours at 370°C, followed by cofeeding 30 ccm of HF and 30 ccm of nitrogen for 18 hours at 370°C. Subsequently, a mixture of 20 ccm of 245fa and 3 ccm of air (equal to about 3 volume % of oxygen, based on the 245fa volume) was fed over the catalyst bed at 400°C for a contact time of 45 seconds. Conversion was 96.2%. Selectivity for the desired (1234ze) product was about 96.3% (about 18.5% cis, about 77.8% trans). Performance of the catalyst was steady for 360 hours.

[0008] Example 2. Example 1 was repeated using $\text{Cr}/\text{Ni}/\text{AlF}_3$ catalyst (activated at 370°C. using a cofeed of 30 ccm of nitrogen and 30 ccm of HF for 18 hours) in a series of 3 tests, using the same temperature and air/245fa feed ratio, but with the contact time between 26 and 39 seconds. Conversions ranged from 88 to 94.5%. Selectivity for the desired (1234ze) product ranged from 96.2 to 98.5% (17.7 to 20.5% cis, 77 to 80.5% trans).

Claims

1. A process for the preparation of cis/trans 1,1,1,3-tetrafluoro-2-propene which comprises (a) contacting 1,1,1,3,3-pentafluoropropane with an oxygen-containing gas in the presence of a fluorided catalyst selected from Cr_2O_3 and $\text{Cr}/\text{Ni}/\text{AlF}_3$, and (b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.
2. A process as in Claim 1 wherein the catalyst is fluorided Cr_2O_3 .
3. A process as in Claim 1 wherein the catalyst is fluorided $\text{Cr}/\text{Ni}/\text{AlF}_3$.
4. A process as in any one of claims 1 to 3 in which the oxygen-containing gas is air.
5. A process as in any of the preceding claims in which the level of oxygen in an organic feed to the catalyst is from 1 to 10vol% based on the volume of the organic feed.

6. A process as in claim 5 in which said level of oxygen is from 2 to 5vol%.
7. A process as in any one of the preceding claims in which the temperature is from 300°C to 400°C.
8. A process as in any one of the preceding claims in which the contact time, defined as total rate of flow divided by volume of catalyst, is from 20 to 50s.
9. A process as in any one of the preceding claims in which the fluorided catalyst is activated before use.

Patentansprüche

1. Verfahren zur Herstellung von cis/trans-1,1,1,3-Tetrafluor-2-propen, umfassend (a) Kontaktierung von 1,1,1,3,3-Pentafluorpropan mit einem Sauerstoffenthaltenden Gas in Gegenwart eines fluoridierten Katalysators, ausgewählt aus Cr_2O_3 und Cr/Ni/AlF_3 , und (b) Gewinnung von cis/trans-1,1,1,3-Tetrafluor-2-propen aus dem resultierenden Reaktionsgemisch.
2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet**, dass der Katalysator fluoridiertes Cr_2O_3 ist.
3. Verfahren nach Anspruch 1, **dadurch gekennzeichnet**, dass der Katalysator fluoridiertes Cr/Ni/AlF_3 ist.
4. Verfahren nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet**, dass das Sauerstoffenthaltende Gas Luft ist.
5. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet**, dass der Sauerstoffgehalt in der organischen Beschickung für den Katalysator 1 bis 10 Vol.-%, bezogen auf das Volumen der organischen Beschickung, beträgt.
6. Verfahren nach Anspruch 5, **dadurch gekennzeichnet**, dass der Sauerstoffgehalt 2 bis 5 Vol.-% beträgt.
7. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet**, dass die Temperatur 300°C bis 400°C beträgt.
8. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet**, dass die Kontaktzeit, definiert als Gesamtrate des Flusses, dividiert durch das Katalysatorvolumen, 20 bis 50 s beträgt.
9. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet**, dass der fluori-

dierte Katalysator vor dem Gebrauch aktiviert wird.

Revendications

1. Procédé pour la préparation de cis/trans-1,1,1,3-tétrafluoro-2-propène, qui comprend les étapes consistant (a) à mettre en contact du 1,1,1,3,3-pentafluoropropane avec un gaz contenant de l'oxygène en présence d'un catalyseur fluoré choisi entre Cr_2O_3 et Cr/Ni/AlF_3 , et (b) à recueillir le cis/trans-1,1,1,3-tétrafluoro-2-propène à partir du mélange réactionnel résultant.
2. Procédé suivant la revendication 1, dans lequel le catalyseur consiste en Cr_2O_3 fluoré.
3. Procédé suivant la revendication 1, dans lequel le catalyseur consiste en Cr/Ni/AlF_3 fluoré.
4. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel le gaz contenant de l'oxygène est l'air.
5. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la quantité d'oxygène dans une charge organique d'alimentation amenée au catalyseur est comprise dans l'intervalle de 1 à 10 % en volume sur la base du volume de la charge organique d'alimentation.
6. Procédé suivant la revendication 5, dans lequel ladite quantité d'oxygène est comprise dans l'intervalle de 2 à 5 % en volume.
7. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la température est comprise dans l'intervalle de 300°C à 400°C.
8. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le temps de contact, défini par la vitesse totale d'écoulement divisée par le volume de catalyseur, est compris dans l'intervalle de 20 à 50 s.
9. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le catalyseur fluoré est activé avant utilisation.